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Routes to Regioselective Deuteration of Heteroaromatic Compounds

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Published in:
Inorganic Chemistry

DOI:
[10.1021/ic020226y](https://doi.org/10.1021/ic020226y)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Browne, W. R., O'Connor, C. M., Killeen, J. S., Guckian, A. L., Burke, M., James, P., Burke, M., & Vos, J. G. (2002). Routes to Regioselective Deuteration of Heteroaromatic Compounds. *Inorganic Chemistry*, 41(16), 4245-4251. <https://doi.org/10.1021/ic020226y>

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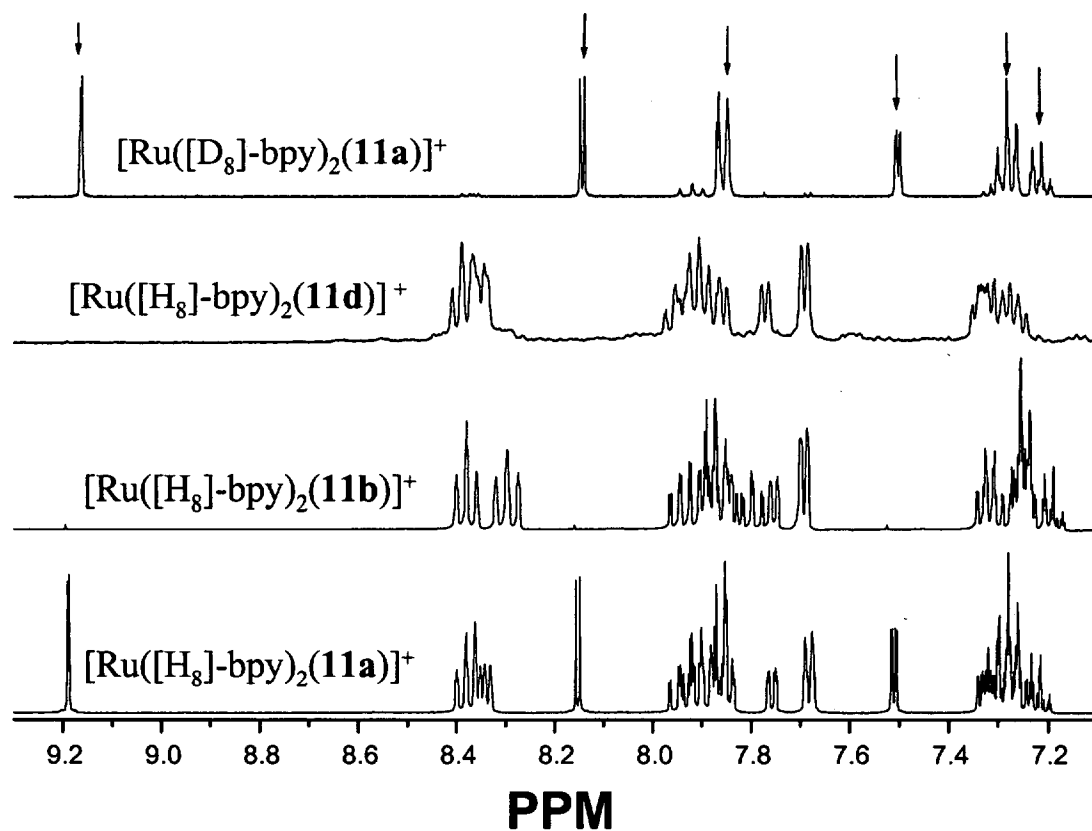
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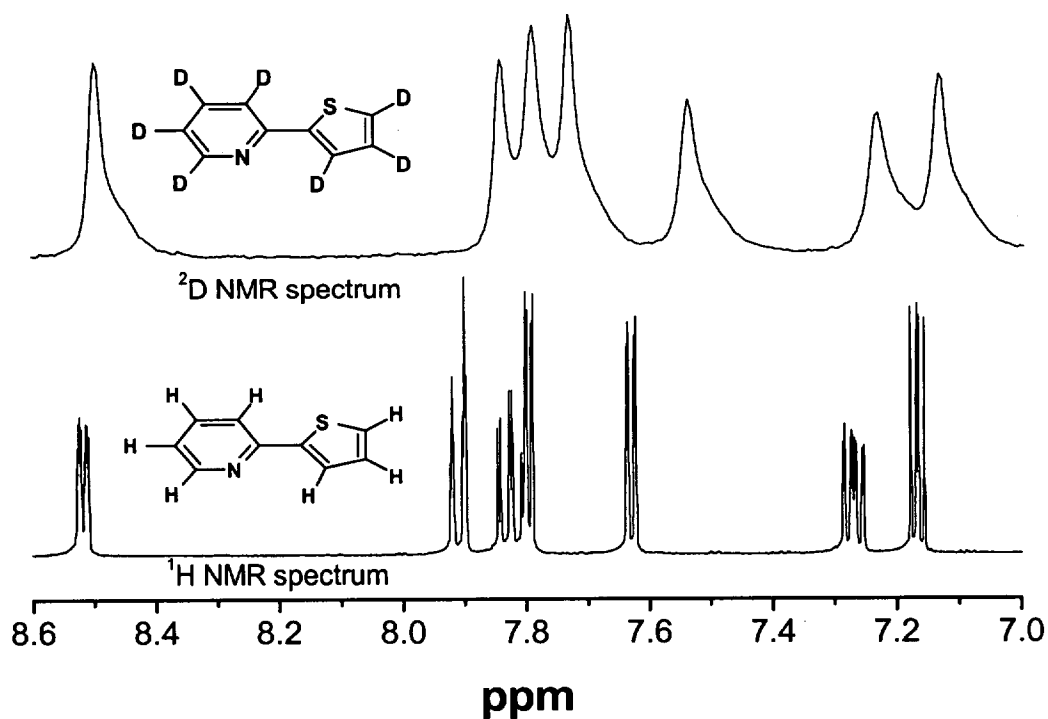
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Supplementary information

(S1) ^1H NMR spectra (400 MHz) of $[\text{Ru}([\text{D}_x]\text{-bpy})([\text{D}_y]\text{-phpztr})](\text{PF}_6)$ in $\text{d}_3\text{-acetonitrile}$ ($x = 0$ or 8 , $y = 0, 3, 8$). phpztr^- (11) resonances are indicated by arrows.



(S2) ^1H NMR spectra of $[\text{H}_7]$ -2-(thein-2'-yl)-pyridine (**8a**) (lower spectrum) in $[\text{D}_6]$ -acetone and ^2D NMR spectra of $[\text{D}_7]$ -2-(thein-2'-yl)-pyridine (**8c**) (upper spectrum) in $[\text{D}_6]$ -acetone



(S3) ^1H , ^2D ^{13}C NMR Spectroscopic data and Mass spectral data for all partially and fully deuteriated compounds described in Tables 1 and 2.

Symmetric Diimine compounds

[D₈]-2,2'-bipyridine **1b**: Mass spectroscopy HM^+ ion at 165 m/z. ^1H NMR in [D₆]-DMSO δ ppm; 8.69 (H3, *resid.* s), 8.39 (H6, *resid.* s), 7.95 (H4, *resid.* s), 7.45 (H5, *resid.* s). ^{13}C NMR in [D₆]-DMSO δ ppm; 149.62 (C3, t), 120.79 (C6, t), 137.68 (C4, t), 124.56 (C5, t), 155.54 (C2, s). ^2D NMR in [H₆]-acetone δ ppm; 8.68 (D3), 8.5 (D6), 7.89 (D4), 7.39 (D5)

[D₄]-4,4'-bipyridine **2b**: Mass spectroscopy HM^+ ion at 161 m/z. ^1H NMR in [D₆]-DMSO δ ppm; 8.72 (H2, *resid.* s), 7.82 (H3, s). ^{13}C NMR in [D₆]-DMSO δ ppm; 150.89 (C2/6, t), 121.64 (C3/5, s), 144.67 (C4, s). ^2D NMR in [H₆]-acetone δ ppm; 8.71 (H2/H6, s), 7.76 (H3/H5, *resid.* s).

[D₈]-4,4'-bipyridine **2c**: Mass spectroscopy HM^+ ion at 165 m/z. ^1H NMR in [D₆]-DMSO δ ppm; 8.72 (H2/6, *resid.* s), 7.82 (H3/5, *resid.* s). ^{13}C NMR in [D₆]-DMSO δ ppm; 150.89 (C2/6, t), 121.64 (C3/5, t), 144.67 (C4, s). ^2D NMR in [H₆]-acetone δ ppm; 8.71 (H2/H6, s), 7.76 (H3/H5, s)

[D₁₂]-4,4'-dimethyl-2,2'-bipyridine **3b**: Mass spectroscopy HM^+ ion at 197 m/z. ^1H NMR in [D₆]-DMSO δ ppm; 2.36 (Me, m), 8.51 (H6, *resid.* s), 8.20 (H3, *resid.* s), 7.27 (H5, *resid.* s). ^{13}C NMR in [D₆]-DMSO δ ppm; 149.32 (C6, t), 121.58 (C3, t), 148.28 (C4, s), 125.25 (C5, t), 155.45 (C2, s), 21.23 (Methyl-, not observed). ^2D NMR in [H₆]-acetone δ ppm; 2.35 (CD₃-), 8.49 (D6), 8.29 (D3), 7.21 (D5).

[D₈]-1,10-phenanthroline **4b**: Mass spectroscopy HM⁺ ion at 189 m/z. ¹H NMR in [D₆]-DMSO δ ppm ; 9.10(H2/9, *resid.* s), 7.77(H3/8, *resid.* s), 8.49 (H4/7, *resid.* s), 7.99 (H5/6, *resid.* s). ¹³C NMR in [D₆]-DMSO δ ppm; 150.31 (C2/9, t), 123.70 (C3/8, t), 136.58 (C4/7, t), 127.04 (C5/6, t), 128.75 (C11/13, s), 145.83 (C12/14, s). ²D NMR in [H₆]-acetone δ ppm; 8.66 (D2/9), 8.46 (D4/7), 7.64 (D5/6 and D3/8))

[D₆]-4,7-diphenyl-1,10-phenanthroline **5b**: Mass spectroscopy HM⁺ ion at 339 m/z. ¹H NMR in [D₆]-chloroform δ ppm ; 9.36 (H2/9, *resid.* s), 7.70 (H3/8, *resid.* s), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, s).

[D₁₀]-4,7-diphenyl-1,10-phenanthroline **5c**: Mass spectroscopy HM⁺ ion at 343 m/z. ¹H NMR in [D₆]-chloroform δ ppm ; 9.36 (H2/9, d), 7.70 (H3/8, d), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, s).

[D₁₄]-4,7-diphenyl-1,10-phenanthroline **5d**: Mass spectroscopy HM⁺ ion at 347 m/z. ¹H NMR in [D₆]-chloroform δ ppm ; 9.36 (H2/9, *resid.* s), 7.70 (H3/8, *resid.* s), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, s). ²D NMR in [H₆]-acetone δ ppm; 9.2 (D2/9), 7.91 (D3/8), 7.63 (phenyl-4/7, *resid.* D5/6)

[D₁₆]-4,7-diphenyl-1,10-phenanthroline **5e**: Mass spectroscopy HM⁺ ion at 349 m/z. ¹H NMR in [D₃]-chloroform δ ppm; 9.36 (H2/9, *resid.* s), 7.70 (H3/8, *resid.* s), 7.64 (phenyl-4,7, *resid.* s), 7.96 (H5/6, *resid.* s). ²D NMR in [H₆]-acetone δ ppm; 9.2 (D2/9), 7.91 (D3/8), 7.63 (phenyl-4/7, D5/6)

[D₁₂]-2,2'-biquinoline **6b**: Mass spectroscopy HM⁺ ion at 269 m/z. ¹H NMR in [D₆]-DMSO δ ppm; 7.69 (*resid. s*), 7.86 (*resid. s*), 8.08 (*resid. s*), 8.19 (*resid. s*), 8.58 (*resid. s*), 8.71 (*resid. s*).

[D₄]-2,2'-biquinoline **6c**: Mass spectroscopy HM⁺ ion at 261 m/z. ¹H NMR in [D₆]-DMSO δ ppm; 7.69 (dd), 7.86 (dd), 8.08 (d), 8.19 (d), 8.58 (*resid. s*), 8.71 (*resid. s*).

Pyrazinyl- and thienyl- pyridine compounds

[D₁₀]-2,3-Di-(pyrid-2yl)-pyrazine **7b**: Mass spectroscopy HM⁺ ion at 245 m/z. ¹H NMR in [D₆]-acetone δ ppm ; 8.79 (pz, *resid. s*), 8.25 (pyH6, *resid. s*), 7.86 (pyH3, *resid. s*), 7.91 (pyH4, *resid. s*), 7.32 (pyH5, *resid. s*). ¹³C NMR in [D₆]-acetone δ ppm; 143.14 (pzC5/6, t), 152.1 (pzC2/3, s), 148.49 (pyC6, t), 124.16 (pyC3, t), 137.13 (pyC4, t), 123.56 (pyC5, t), 157.2 (C2, s). ²D NMR in [H₆]-acetone δ ppm; 8.71 (pz), 8.21 (pyD6), 7.88 (pyD3/D4), 7.27 (pyD5)

[D₂]-2-(thien-2'-yl)-pyridine **8b**: Mass spectroscopy M⁺ ion at 164 m/z. (thH3,d), (thH4,d), (thH5, *resid. s*), (pyH6, *resid. s*), (pyH3,d), (pyH4,dd), (pyH5,d). ¹³C NMR in [D₆]-acetone δ ppm; 144.87 (thC2,s), 125.56 (thC3, s), 128.70(thC4,s), 128.77(thC5,t), 152.15 (pyC2,s), 118.99 (pyC3,s), 137.53(pyC4,s), 122.69 (pyC5,s), 149.70 (pyC6,t). ²D NMR in [H₆]-acetone δ ppm; 7.72 (*resid. thD3 ~ 15%*), 7.54 (thD5), 8.50 (pyD6).

[D₇]-2-(thien-2'-yl)-pyridine **8c**: Mass spectroscopy M⁺ ion at 169 m/z. ¹H NMR in [D₆]-acetone δ ppm ; 7.7 (thH3, *resid. s*), 7.1 (thH4, *resid. s*), 7.6 (thH5, *resid. s*), 8.5 (pyH6, *resid. s*), 7.9 (pyH3, *resid. s*), 7.8 (pyH4, *resid. s*), 7.2 (pyH5, *resid. s*). ¹³C NMR in [D₆]-acetone δ ppm; 144.87 (thC2,s),

125.56 (thC3,t), 128.70(thC4,t), 128.77(thC5,t), 152.15 (pyC2,s), 118.99 (pyC3,s), 137.53(pyC4,s), 122.69 (pyC5,s), 149.70 (pyC6,s). ^2D NMR in $[\text{H}_6]$ -acetone δ ppm; 7.73 (thD3), 7.13 (thD4), 7.54 (thD5), 8.50 (pyD6), 7.84 (pyD3), 7.79 (pyD4), 7.23 (pyD5).

Pyrazine-1,2,4-triazole based compounds

$[\text{D}_4]$ -Hpztr **9b**: Mass spectroscopy HM^+ ion at 152 m/z. ^1H NMR ($[\text{D}_6]$ -DMSO) δ in ppm: 9.46 (*resid.* s, pz-H3), 8.70 (*resid.* s, pz-H5), 8.66 (*resid.* s, pz-H6), 8.25 (*resid.* s, tr-H5), ^2D NMR in ($[\text{H}_6]$ -DMSO) δ ppm; 9.24 (pz-D3), 8.72 (pz-D5/D6), 8.49 (tr-D5)

$[\text{D}_6]$ -Hmepztr **10b**: Mass spectroscopy HM^+ ion at 169 m/z. ^1H NMR ($[\text{D}_6]$ -DMSO) δ in ppm: (*resid.* s, pz-H3), (*resid.* s, pz-H5), (*resid.* s, pz-H6), (*resid.* m, Methyl). ^2D NMR in ($[\text{H}_6]$ -DMSO) δ ppm; 9.07 (pz-D3), 8.63 (pz-D5/D6), 2.32 (Methyl)

$[\text{D}_3]$ -Hphpztr **11b**: Mass spectroscopy HM^+ ion at 227 m/z. ^1H NMR ($[\text{D}_6]$ -DMSO) δ in ppm: 9.35 (*resid.* s, pz-H3), 8.795 (*resid.* s, pz-H5), 8.765 (*resid.* s, pz-H6), 8.11 (d, 2H, ph-H2/H6), 7.54 (dd, 2H, ph-H3/H5) 7.49 (t, 1H, ph-H4). ^2D NMR in ($[\text{H}_6]$ -DMSO) δ ppm; 9.33 (pz-D3), 8.75 (pz-D5/D6)

$[\text{D}_5]$ -Hphpztr **11c**: Mass spectroscopy HM^+ ion at 229 m/z. ^1H NMR ($[\text{D}_6]$ -DMSO) δ in ppm: 9.35 (d, 1H, pz-H3), 8.795 (dd, 1H, pz-H5), 8.765 (d, 1H, pz-H6), 8.11 (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4), ^2D NMR in ($[\text{H}_6]$ -DMSO) δ ppm; 8.07 (ph-D2/D6), 7.48 (ph-D3/D4/D5)

[D₈]-Hphpztr **11d**: Mass spectroscopy HM⁺ ion at 332 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 9.35 (*resid.* s, pz-H3), 8.795 (*resid.* s, pz-H5), 8.765 (*resid.* s, pz-H6), 8.11 (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4). ²D NMR in ([H₆]-DMSO) δ ppm; 9.33 (pz-D3), 8.75 (pz-D5/D6), 8.07 (ph-D2/D6), 7.48 (ph-D3/D4/D5).

[D₃]-Htolpztr **12b**: Mass spectroscopy HM⁺ ion at 241 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 9.33 (*resid.* s, pz-H3), 8.77 (*resid.* s, pz-H5/H6), 7.34 (d, 2H, ph-H2/H6), 8.00 (dd, 2H, ph-H3/H5), 2.36 (s, 3H, -CH₃). ²D NMR in ([H₆]-DMSO) δ ppm; 9.34 (pz-D3), 8.74 (pz-D5/D6)

[D₃]-Htolpztr **12c**: Mass spectroscopy HM⁺ ion at 241 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 9.33 (d, 1H, pz-H3), 8.77 (m, 2H, pz-H5/H6), 7.34 (d, 2H, ph-H2/H6), 8.00 (dd, 2H, ph-H3/H5), 2.36 (*resid.* m, methyl). ²D NMR in ([H₆]-DMSO) δ ppm; 2.28 (Methyl-)

[D₄]-Htolpztr **12d**: Mass spectroscopy HM⁺ ion at 242 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: (d, 1H, pz-H3), (dd, 1H, pz-H5), (d, 1H, pz-H6), (*resid.* s, ph-H2/H6), (*resid.* s, ph-H3/H5), (s, 3H, methyl).

[D₆]-Htolpztr **12e**: Mass spectroscopy HM⁺ ion at 244 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 9.33 (*resid.* s, pz-H3), 8.77 (*resid.* s, pz-H5/H6), 7.34 (d, 2H, ph-H2/H6), 8.00 (dd, 2H, ph-H3/H5), 2.36 (*resid.* m, methyl). ²D NMR in ([H₆]-DMSO) δ ppm; 9.34 (pz-D3), 8.74 (pz-D5/D6), 2.28 (Methyl-).

[D₇]-Htolpztr **12f**: Mass spectroscopy HM⁺ ion at 245 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 9.33 (d, 1H, pz-H3), 8.77 (m, 1H, pz-H5/H6), 7.34 (*resid.* s, ph-H2/H6), 8.00 (*resid.* s, ph-H3/H5) 2.36 (*resid.* m, methyl).

[D₁₀]-Htolpztr **12g**: Mass spectroscopy HM⁺ ion at 248 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 9.33 (*resid.* s, pz-H3), 8.77 (*resid.* s, pz-H5), (*resid.* s, pz-H6), 7.34 (*resid.* s, ph-H2/H6), 8.00 (*resid.* s, ph-H3/H5), 2.36 (*resid.* m, methyl)

Pyridine-1,2,4-triazole based compounds

[D₅]-Hpytr **13b**: Mass spectroscopy HM⁺ ion at 151 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: 8.09 (*resid.* s, py-H3), 7.98 (*resid.* s, py-H4), 7.51 (*resid.* s, py-H5), 8.70 (*resid.* s, py-H6), 8.27 (*resid.* s, tr-H5). ²D NMR in ([H₆]-DMSO) δ ppm; 7.99 (py-D3), 7.88 (py-D4), 7.51 (py-D5), 8.71 (D6), 8.12 (tr-D5)

[D₇]-Hmepyr **14b**: Mass spectroscopy HM⁺ ion at 168 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: (*resid.* s, py-H3), (*resid.* s, py-H4), (*resid.* s, py-H5), (*resid.* s, py-H6), (*resid.* m, Methyl). ²D NMR in ([H₆]-DMSO) δ ppm; 7.96 (py-D3), 7.84 (py-D4), 7.38 (py-D5), 8.58 (py-D6), 2.26 (Methyl)

[D₁]-Hphpytr **15b**: Mass spectroscopy HM⁺ ion at 224 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: (d, 1H, py-H3), (dd, 1H, py-H4), (dd, 1H, py-H5), (*resid.* s, py-H6), (d, 2H, ph-H2/H6), 7.54 (dd, 2H, ph-H3/H5) 7.49 (t, 1H, ph-H4), ²D NMR in ([H₆]-DMSO) δ ppm; 8.67 (py-D6)

[D₄]-Hphpytr **15c**: Mass spectroscopy HM⁺ ion at 227 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: (*resid.* s, py-H3), (*resid.* s, pz-H4), (*resid.* s, py-H5), (*resid.* s, py-H6), (d, 2H, ph-H2/H6), 7.54 (dd, 2H, ph-H3/H5) 7.49 (t, 1H, ph-H4), ²D NMR in ([H₆]-DMSO) δ ppm; 8.09 (py-H3/H4), 7.49 (py-H5), 8.70 (py-H6).

[D₅]-Hphpytr **15d**: Mass spectroscopy HM⁺ ion at 228 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: (d, 1H, py-H3), (dd, 1H, py-H4), (dd, 1H, py-H5), (d, 1H, py-H6), (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4).

[D₉]-Hphpytr **15e**: Mass spectroscopy HM⁺ ion at 232 m/z. ¹H NMR ([D₆]-DMSO) δ in ppm: (*resid.* s, py-H3), (*resid.* s, py-H4), (*resid.* s, py-H5), (*resid.* s, py-H6), (*resid.* s, ph-H2/H6), 7.54 (*resid.* s, ph-H3/H5) 7.49 (*resid.* s, ph-H4). ²D NMR in ([H₆]-DMSO) δ ppm; 8.08 (py-H3/H4), 7.48 (py-H5, ph-H3/H5/H4), 8.70 (py-H6), 8.01 (ph-H2/H6).